

Final Report
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TROPOSPHERIC OH, HO₂, AND NO BY RESONANCE EMISSION:
INSTRUMENTATION AND MEASUREMENT OF ABUNDANCES AND FLUXES

submitted to

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Introduction

Key to understanding tropospheric oxidation are measurements of OH and HO₂ and measurements of NO₂ (Albritton et al., 1990; Crosley, 1993a,b). In the free troposphere, OH and HO₂ formation and reactions are the main sink of ozone. OH and HO₂ interact with NO_x, CO, and hydrocarbons to determine the production or loss of ozone. The OH concentration in the free troposphere determines the atmospheric lifetimes of many chemical species, including greenhouse gases such as methane and contributors to stratospheric ozone loss such as the HCFCs.

Previous attempts to measure OH were too insensitive or had significant interferences. Current techniques for measuring NO₂ have artifacts that limit the minimum detectable mixing ratio to about 10 pptv. Measurements of NO₂ with current techniques is the primary suspect in the differences between the measured and modeled NO₂/NO ratio. These problems with previous and current measurement techniques motivated us to propose the development of spectroscopic techniques for OH and NO₂, and chemical conversion of HO₂ to OH followed by spectroscopic detection.

Summary of research for NASA grant NAG1-1057

NASA grant NAG1-1057 (October, 1989-April, 1996) and NSF grants ATM-8909155 (April, 1990-September, 1993) and ATM-9217748 (May, 1993-October, 1996) jointly supported our development of instrumentation to measure tropospheric OH and HO₂ and tropospheric NO₂. The goal was to develop, deploy, and test instrumentation on the ground, and then to use what was learned about this instrumentation to build instrumentation for aircraft measurements throughout the troposphere. While we were only able to demonstrate the promise of the NO₂ instrumentation for sampling in the remote troposphere, we did successfully build and deploy instrumentation to measure OH and HO₂ from the NASA DC-8 aircraft. The bulk of the funds to build the aircraft instrument came from NASA grant NAG2-938 and USDC/NOAA grant NA56GP0179; however, the instrument evolved from the instrumentation development supported by this grant.

During the first three years, we developed our version of the FAGE-type instrument for measuring OH and HO₂. In a FAGE-type instrument, a pulsed laser illuminates the air sample as it flows through a detection chamber. The laser wavelength is tuned to coincidence with one of the molecule's absorption peaks, and the molecule radiates some of this absorbed energy isentropically. A detector set at right angles to the air flow and the laser light detects this faint fluorescence. The fluorescence is separated from the laser scattering off of the chamber walls and air by turning the detector on to collect some of the fluorescence only after the laser pulse has left the chamber.

Our instrument can be capable of detecting less than 2×10^5 OH molecules cm⁻³ in 1 minute sampling time. Initially, we used an Oxford Lasers copper vapor laser pumping a Lambda Physik 3001 dye laser as the light source and a fast, gated microchannel plate detector for fluorescence detection. In tests on the roof of the Walker Building at Penn State University in 1992, this instrument measured OH with good signal-to-noise ratio, specificity, and freedom from interferences (Stevens et al., 1994). The HO₂ mixing ratio was measured easily. Buoyed by the success of this rapid development, we sought to test this instrument under field conditions as soon as possible.

ROSE II Participation and Results. Near the end of the first 3 years, we were given the opportunity to participate in the Rural Oxidants in the Southern Environment II (ROSE II) experiment in southwestern Alabama, in June, 1992. The canopy of the surrounding forest was at 12 meters, and we set the detection axis at 8 meters while the laser and electronics stayed on the ground. Between the optical instability of this arrangement and the rapid decay of laser dye in the Alabama heat, we obtained only a few, low quality OH measurements. However, HO₂ measurements were frequent and high quality.

The main result of the measurement in ROSE II was that the mixing ratios of both OH and HO₂ are less than calculated from photochemical models constrained by simultaneous measurements of other chemical species and meteorology (Perkowski, 1995). Midday OH concentrations were typically $< 2 \times 10^6$ cm⁻³, uncertain by a factor of 2. Most surprisingly, measured, midday HO₂ mixing ratios were 3 to 8 pptv, not 30 to 50 pptv as calculated from measurements of RO₂+HO₂ by the chemical amplifier technique made during ROSE I (Cantrell et al., 1993).

Results from the second 3 years. The main goal of the second 3 years was to further test the OH/HO₂ instrument, including informal intercomparisons, and to begin contributing to the understanding of tropospheric oxidation by local measurements and participation in multi-investigator experiments. An additional aspect of this grant was to develop the use of a smaller, lighter laser system, one that could then become a component of an aircraft instrument. Third was further NO₂ sensor development, which had only just begun in the first 3 years.

TOHPE Participation and Results. In August and September, 1993, we participated in the Tropospheric OH Photochemistry Experiment (TOHPE) at Idaho Hill, Colorado, 17 miles east of Boulder, CO. For our instrument, the laser and electronics were in a trailer and the detection axis was firmly attached on a tower to the trailer's side for better optical stability than we had in Alabama.

We used a copper laser pumping a dye laser designed and successfully used by Harvard University in their HO_x instrument on the NASA ER-2 aircraft (Wennberg et al., 1994). Unfortunately, neither our Harvard colleagues nor we realized the problems with this combination until they appeared: the operational UV laser power out of the dye laser was 50 times smaller than expected, the laser operated in more than one mode simultaneously, and the "background signal" was 100 times greater than we observed with the Lambda Physik dye laser because of the long decay time of the Harvard dye laser. OH measurements were made difficult, but the HO₂ measurements were only slightly affected.

The results of our OH and HO₂ measurements from TOHPE are very similar to our measurements from ROSE II. The poor laser performance precluded a meaningful comparison with the chemical ionization/mass spectrometer technique and limited the total number of measurements to less than 30 over the six week long period. However, two aspects are encouraging. First, on 20 September, our OH measurements mimicked the chemical ionization/mass spectroscopy measurements as pollution penetrated the site just after noon (Figure 1). Second, the average value of our all our measurements, with a 1 σ uncertainty of 40% and factor of 2 uncertainty, is about 70% of the average value of the chemical ionization/mass spectrometer measurements for the same time periods.

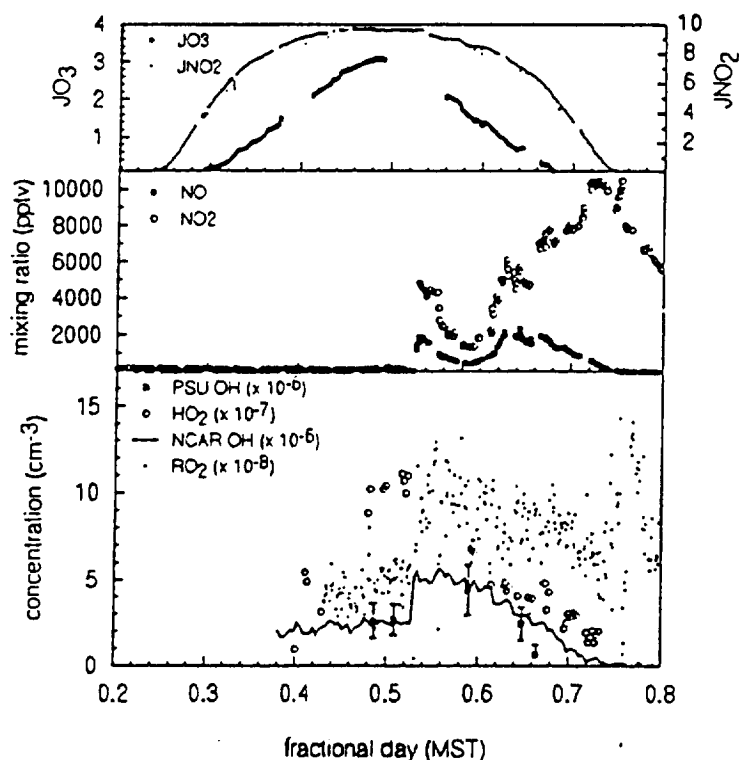


Figure 1. Observations of OH, HO₂, RO₂, NO, NO₂, JNO₂, and J_O₃ from TOHPE for 20 September 1993. Pollution event occurred about 12:30. Error bars on PSU OH are 1 σ precision. (from Stevens et al. submitted to J. Geophys. Res., 1995)

Measurements of HO₂ mixing ratios were made on 16 days of the 21 possible. Typical peak midday values were 5 to 9 pptv, similar to those measured during ROSE II (Figure 2). These values are a factor of 3 to 6 below model calculations in clean air, but agreed with model calculations in polluted air (Cantrell et al., submitted 1995; McKeen et al., submitted 1995). Peak midday RO₂ + HO₂ values are typically 25 to 40 pptv, except during pollution episodes, when they approximately double. In addition, the HO₂/OH ratio was typically 50-100, whereas model calculations would suggest ratios of 150 to 300. The measured RO₂/HO₂ ratio was typically 5 to 10, whereas model calculations suggest ratios closer to 1. These differences all result from differences between measured and calculated HO₂.

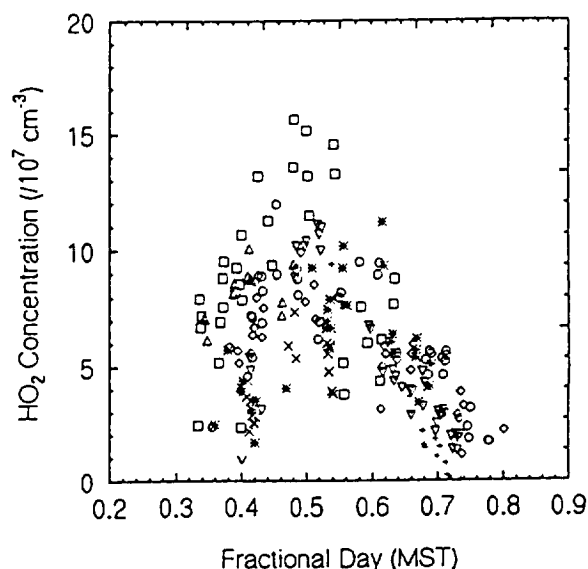


Figure 2. HO₂ measurements during TOHPE in August and September 1993. Each symbol represents a different day. Because the air density was about $2 \times 10^{19} \text{ cm}^{-3}$ at Idaho Hill, CO, the maximum observed mixing ratio was 8 pptv. (from Mather et al., accepted by J. Geophys. Res., 1995)

Diagnostic measurements made during TOHPE confirm that the instrument was operating correctly, although the absolute sensitivity was uncertain by a factor of 2. First, when H₂O in ambient air was dissociated by 185 nm radiation from an Hg lamp, the observed HO₂ concentration equaled the observed OH concentration. This equality is expected because $\text{H}_2\text{O} + h\nu(185 \text{ nm}) \rightarrow \text{H} + \text{OH}$ is followed by $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$ to make equal parts of OH and HO₂. Second, when NO was added externally to the low pressure sampling flow tube, RO₂ and HO₂ should both be converted to OH. However, the conversion is not 100% because the resulting OH reacts with NO to form HONO rapidly. Calculations suggest that observed OH should be at most 32% of the initial RO₂ + HO₂. Thus, using this conversion efficiency, we observe a minimum value of RO₂ + HO₂ of 22 pptv, while the observed value was closer to 50 pptv. Because we were unlikely to match the reaction time and NO concentration necessary to attain even 32% conversion, these two signals can be considered to be roughly in agreement.

Modeling studies of non-methane hydrocarbon oxidation. Several possibilities for the large differences between the observed and calculated HO₂ mixing ratios have been proposed. Among these are heterogeneous chemistry of HO₂ (Cantrell et al., 1995), more rapid than expected removal of OH, and incorrect oxidation pathways or rates for non-methane hydrocarbon oxidation. We chose to do sensitivity studies of this last possibility. We use a steady-state photochemical model developed by Donahue and Prinn (1990) for the marine boundary layer and adapted it to our conditions. This model was chosen because we could modify the individual steps in the oxidation pathways of each hydrocarbon.

For both ROSE II and TOHPE, isoprene is an important NMHC. In our sensitivity study, we lower the rate of $\text{RO}_2 + \text{NO} \rightarrow \text{products}$ by a factor of 10 and raise the $\text{RO}_2 + \text{HO}_2 \rightarrow \text{products}$ rate by a factor of 5 for isoprene oxidation. Both of these changes are consistent with the suggestions from laboratory studies (Peeters et al., 1992). With these changes, the amounts of OH, HO_2 , and RO_2 can be better matched than with standard chemistry. However, the calculated photostationary state of NO_2 and NO, which often requires more oxidant than observed to match observations, deviates even somewhat more from the observations. The implications of these changes for isoprene oxidation chemistry is that natural hydrocarbons such as isoprene may be less effective than other hydrocarbons at producing ozone.

Developing an NO_2 sensor. The excitation spectrum of NO_2 between 550 nm and 600 nm consists of several sharp features above a continuum (Hsu et al., 1978). For the stronger lines, the ratio of the absorption on-line to off-line is a factor of 3 to 5. The fluorescence extends from the excitation wavelength into the infrared (Donnelly et al., 1979). On the other hand, the fluorescence is quickly quenched, so that the fluorescence pulse mimics the laser pulse, even at pressures as low as 1 hPa. Thus, the NO_2 detection can be based upon excitation near 560 - 585 nm, tuning on and off narrow absorption features, and detection at wavelengths longer than 700 nm.

We have developed an instrument based on these principles and the hardware from the OH detection system. The laser is a etalon-narrowed (0.04 cm^{-1}) Lambda Physik dye laser that is pumped by an Oxford Lasers pulsed copper laser. This laser beam, about 200 to 750 mW, is multi-passed with a White cell through the ambient airstream in a detection chamber at 5 hPa and the NO_2 fluorescence is detected at right angles to both the flow and the laser beam. Optical filters separate the NO_2 fluorescence beyond 700 nm from the excitation laser, and a cooled PMT is the detector.

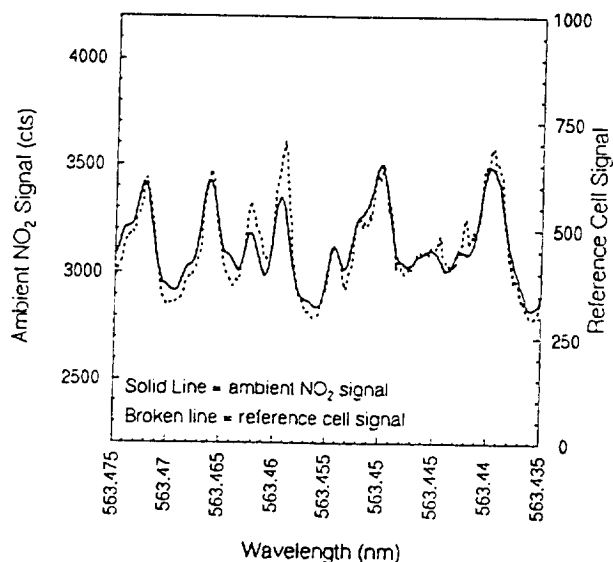


Figure 3. Spectra of NO_2 in the air (solid line) and in a reference cell (broken line) for 5 November on the roof of Walker Building. Laser wavelength is scanned to get the spectra. Good agreement between spectra implies that interferences from other chemical species are small. Small disagreements, possibly resulting from changing NO_2 during the scan, statistical noise, laser variation, or other species, are being investigated. This wavelength scan took 20 minutes.

Measurements have recently been made from the roof of Walker Building at Penn State University (Figures 3 and 4). The spectrum of NO_2 is basically the same in ambient air and the NO_2 reference cell. The sensitivity is calibrated by adding a known amount of NO_2 to zero air, and is 0.024 cts s^{-1} per pptv of NO_2 for the laser power used in the measurements. With a background signal of 3000 cts s^{-1} , the detection limit

of this instrument is 850 pptv for $S/N = 2$ and an integration time of 2 minutes (1 minute on line and one minute off). The NO_2 measurements consist of on-peak and off-peak measurements (Figure 4a). The difference signal is proportional to the NO_2 mixing ratio (Figure 4c). These measurements show promise for this technique, although the sensitivity and background signals both still require work.

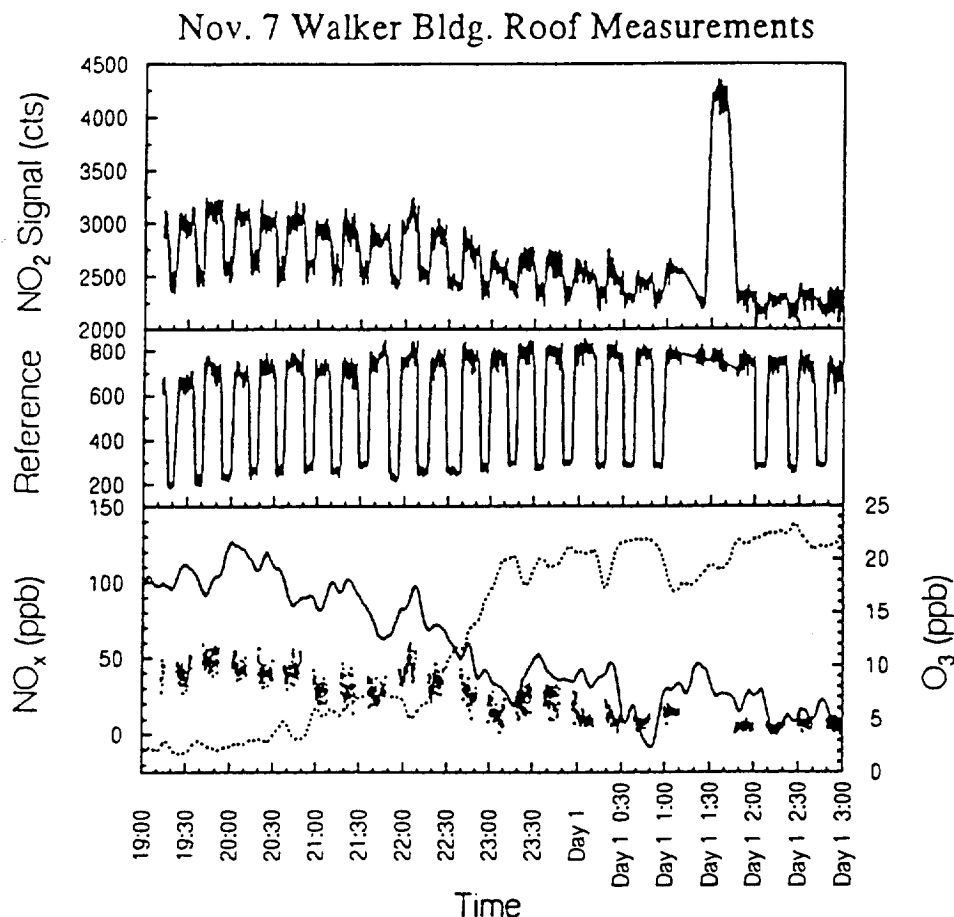


Figure 4. Evening and nighttime measurements of NO_2 by LIF, and NO , and O_3 for 7 November from the roof of the Walker Building. The top panel is the raw signal, 10 second averages, with the laser tuned on and off resonance, as indicated by the NO_2 reference cell (middle panel). Large feature is a calibration with 93 ppbv of NO_2 . Bottom panel shows NO_2 (dots), NO (solid line) and O_3 (dotted line).

Development of ATHOS (Airborne Tropospheric Hydrogen Oxides Sensor)

Strictly speaking, the development of ATHOS was funded by other grants. However, because this airborne HO_x is a direct product of this NASA grant, and because it was a major goal of this grant, we devote in this summary some discussion of its design, capabilities, and measurements during the SUCCESS campaign over the central United States in April-May, 1996.

This instrument uses laser induced fluorescence in detection cells at low pressure to detect OH. HO_2 is first converted to OH by a fast chemical reaction with NO and then detected by LIF. The laser system consists of a Lightwave Electronics model 210G diode-pumped Nd:YAG laser that pumps the Harvard dye laser. The 210G, which just became available in October 1995, is capable of producing pulses with the following characteristics: average power - 2.3 W; repetition rate - 3 to 10 kHz; pulse length - 40 ns; and pulse-to-pulse

variability - < 5%. This laser is small, relatively lightweight, and consumes less than 800 W electrical power. The Lightwave Laser coupled to the Harvard dye laser gives us about as much laser power as we need for successful airborne tropospheric measurements.

The aircraft instrument, called the Airborne Tropospheric Hydrogen Oxides Sensor (ATHOS), is mounted in the forward cargo bay of the NASA DC-8 aircraft, as shown schematically in Figure 5. A specially designed sampling nacelle has been designed by Kevin James of NASA Ames Research Center to slow the airflow from the aircraft speed of 240 m s^{-1} to 5 m s^{-1} . Air is then drawn into the sampling flow tube and through the OH and HO_2 detection axes. All of the instruments resides in the forward cargo bay - the operators sit in the main cabin with a computer monitor, keyboard, and mouse to control instrument operation.

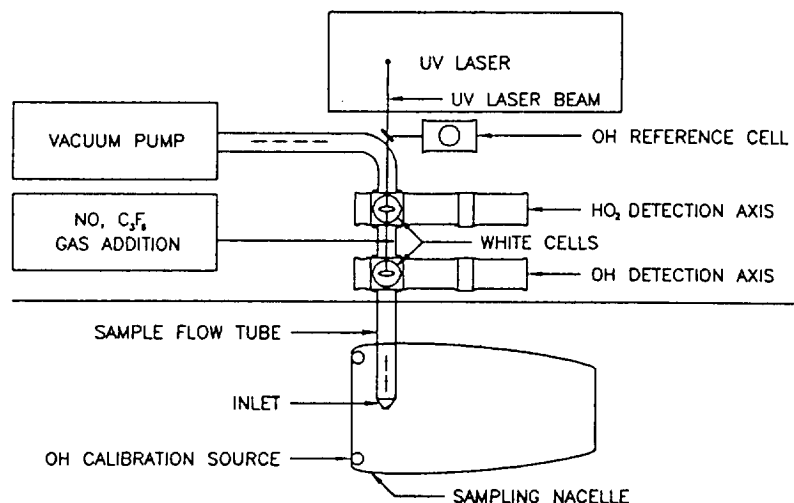


Figure 5. Schematic of ATHOS, showing the orientation on the DC-8, the simultaneous detection of OH and HO_2 , and the sampling arrangement. Not shown are the electronics rack and the details of the sampling nacelle, which consists of two concentric cylindrical tubes shaped like airfoils.

Performance of ATHOS during SUCCESS

Of the 19 flights, ATHOS has observed OH on all flights and HO_2 on 5 flights. All data are recorded at 5 Hz, and statistically significant OH signals are produced in 0.2 seconds in aircraft contrails. Although ATHOS is not yet well-calibrated, preliminary looks at the data suggest the following observations. First, the HO_2 to OH ratio was generally in the range of 10 to 50 for mostly clear-sky conditions. Its dependence on altitude, solar UV, water vapor, NO, and other factors has not yet been determined. Second, in the near-field contrails of both the 757 and the T-39, OH was enhanced above ambient by a factor of 5 to 10, while HO_2 was decreased a factor of 2 to 3. The anticorrelation between OH and HO_2 was strong, although it is not yet clear if the increase in OH was equal to the decrease in HO_2 . Third, in the DC-8 contrails, which were older when observed than the 757 contrails were, the enhancement in OH was typically only a factor of two or three. Laboratory studies will be necessary to guarantee that these enhancements are not instrument artifacts. Fourth, OH was not enhanced in clouds, and after more analysis, may be shown to actually decrease. Last, while determination of OH and HO_2 mixing ratios awaits post-flight calibrations, estimates using a preliminary calibration suggest that the OH mixing ratio is in the range of a few tenths of a pptv and the HO_2 mixing ratio is in the range of a few pptv.

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